

Ground-state properties of rutile: electron-correlation effects

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Electron-correlation effects on cohesive energy, lattice constant and bulk compressibility of rutile are calculated using an *ab-initio* scheme. A competition between the two groups of partially covalent Ti-O bonds is the reason that the correlation energy does not change linearly with deviations from the equilibrium geometry, but is dominated by quadratic terms instead. As a consequence, the Hartree-Fock lattice constants are close to the experimental ones, while the compressibility is strongly renormalized by electronic correlations.

I. INTRODUCTION

Although transition-metal oxides are one of the most interesting classes of solids, relatively little theoretical work aiming at a microscopic understanding of electron-correlation effects in these systems is available so far. This is not surprising: high numerical effort is already required here for accurately describing ground-state properties at the Hartree-Fock (HF) independent-particle level. Recently, results on NiO^{1,2} and on the rutile TiO₂ crystal^{3,4} were published. Correlation effects in TiO₂ have been studied only implicitly, at the density-functional level⁴⁻⁶.

Rutile is one of the experimentally found modifications of TiO₂. The investigation of the relative stability compared to other phases such as anatase, brookite or TiO₂(B) is another interesting subject⁷. Rutile is well studied by experimentalists; the structure was precisely determined by using X-ray and neutron diffraction (for a discussion of the experimental results see Ref. 6 and references therein). The experimental lattice constant is close to values obtained in *ab-initio* self-consistent field (SCF) calculations⁴, whereas the difference between SCF results and experiment for the compressibility is large. This contradiction makes the task of studying electron correlations in the rutile crystal interesting.

From the methodological point of view the rutile crystal is a next logical step in the application of a correlation treatment within the so-called "scheme of local increments"^{8,9}. The validity of this approach was successfully tested for covalently bonded solids like diamond, graphite and many typical semiconductors⁹⁻¹³. For purely ionic crystals the scheme works also well (see references for MgO, CaO, NiO and alkali halides^{14,15,2,16}). II-VI semiconductors have been investigated as an example of partly ionic, partly covalent crystals¹⁷. With respect to this, rutile is another excellent object for testing.

In the present short contribution we report on *ab-initio* correlation calculations for the cohesive energy, lattice constant and compressibility of rutile. The paper is organized as follows. In the second chapter we outline the

computational method and describe our results. We also discuss individual correlation-energy increments and address the question of their transferability when approximating the infinite crystal by embedded clusters. A discussion and a short summary are presented in the last chapter.

II. COMPUTATIONAL METHOD

The rutile structure is tetragonal (nonsymmorphic space group $P4_2/mnm$) with two titanium atoms and four oxygens per primitive unit cell (see Fig. 1). Ti atoms are located at positions $(0, 0, 0)$ and $(1/2, 1/2, 1/2)$ and oxygens at positions $(\pm x, \pm x, 0)$ and $(1/2 \pm x, 1/2 \mp x, 0)$. The lattice constants extrapolated to zero temperature¹⁸ are $a = 4.592 \text{ \AA}$ and $c = 2.958 \text{ \AA}$, the dimensionless coordinate $x = 0.3048$. The experimental value for θ is 98.8° . The bonding and charge distribution in the rutile crystal have been discussed in Ref. 5. The SCF Mulliken population analysis^{3,4} shows that the excess negative charge on oxygen is about $-1.4e$. On Ti, in addition to the closed (but easily deformable) argon-like core the population analysis gives 1.2 valence electrons in the d shell, whereas the $4s$ shell is not occupied^{3,4}.

After this preliminary discussion, we briefly review our theoretical approach for including electron correlation on top of a crystal SCF calculation. The main idea is to expand the total correlation energy, E_{corr} , of the crystal in terms of local correlation-energy increments. Details have been described in previous papers^{8-11,14}. Essentially, we use a Bethe-Goldstone-like hierarchy of the type

$$E_{corr} = \sum_A \varepsilon(A) + \frac{1}{2} \sum_{A,B} \Delta\varepsilon(AB) + \frac{1}{3!} \sum_{A,B,C} \Delta\varepsilon(ABC) + \dots \quad (1)$$

where A, B, C, \dots denote groups of occupied localized orbitals on atoms A, B, C, \dots , respectively (we use the same symbol for an atom and for the group of the localized orbitals on A). The quantity $\varepsilon(A)$ (a one-body increment) denotes the (local) correlation energy of the crystal in which only the orbitals of group A are correlated. The two-body increment $\Delta\varepsilon(AB)$ is defined as the non-additive part of correlations arising from simultaneously correlating the groups A and B :

$$\Delta\varepsilon(AB) = \varepsilon(AB) - \varepsilon(A) - \varepsilon(B) \quad (2)$$

Similarly three-body increments can be introduced as follows:

$$\begin{aligned} \Delta\varepsilon(ABC) &= \varepsilon(ABC) - \Delta\varepsilon(AB) - \\ \Delta\varepsilon(AC) - \Delta\varepsilon(BC) &- \varepsilon(A) - \varepsilon(B) - \varepsilon(C) \end{aligned} \quad (3)$$

Even if one should want to treat these formulae as purely phenomenological ones, still the expansion (if carried out to infinity) is exact which is clear upon inspection. (For a more sophisticated derivation, cf. Ref.

19.) For practical applications, however, some approximations are inevitable. The first approximation consists in truncating the infinite series. The data for various systems^{8–13,17,2,14–16} show that the expansion is quickly convergent. The three-body increments were found to be almost negligible (for the bulk of practical applications). Moreover, two-body increments were found to decay rapidly for larger distances. The second (more serious) approximation for the incremental expansion consists of replacing the infinite crystal with finite embedded clusters for the purpose of determining individual increments. This approximation uses the local nature of electron correlation²⁰ and was found to work well. Note that we restrict the local cluster treatment to correlation effects only — SCF interactions are long-range, and a calculation involving the whole (infinite) lattice is mandatory here. This is possible with the CRYSTAL program package^{21,22}.

Applying the combined scheme just described to TiO_2 , one obtains the total energy functional

$$E_{tot}(a, c, x) = E_{scf}(a, c, x) + E_{corr}(a, c, x) \quad (4)$$

as a function of the lattice parameters a, c, x or r_1, r_2, Θ (in internal coordinates). The crystal compressibility B , at zero temperature, is defined as

$$B = V \frac{\partial^2 E_0(V)}{\partial^2 V} \quad (5)$$

with V denoting the volume of the unit cell and $E_0(V)$ the *conditional* minimum of $E_{tot}(a, c, x)$ for *fixed constant volume*. Using $V = a^2c$ and expressing $E_{tot}(a, V/a^2, x)$ as a function of two independent variables a, x , the compressibility B can be obtained. This method is usually not applied to noncubic crystals, but instead the minimum position at a_0, c_0, x_0 is approached by a conjugated gradient technique. This reduces the number of data points, and the compressibility can only be obtained then by applying an empirical ansatz such as the Murnaghan equation of state (cf. e.g. Ref. 4). Another possibility is to define an *artificial* isotropic compressibility⁴ B_{ISO} where one (incorrectly) assumes that under compression x remains constant and a and c scale isotropically.

A. Basis sets

SCF calculations: For the titanium atom, a relativistic energy-consistent 12-valence-electron pseudopotential²³, together with a 411/411/41 basis set⁴ was used. For oxygen we chose the basis set given by Causà et al²⁴. To calculate the energy of the free atoms, diffuse functions cannot be omitted (let us remind that they must be omitted in CRYSTAL calculations^{21,22}). Thus we appropriately supplemented the basis sets for this purpose²⁵. Our SCF cohesive energy is smaller compared to that of Ref. 4 probably just because of the lack of diffuse functions

for the free Ti atom in Ref. 4. Of course, this omission affected only the cohesive energy.

Correlation calculations: For oxygen we used Dunning’s correlation-consistent augmented valence triple zeta $[5s4p3d2f]$ basis set²⁶. For Ti, our starting point was a $[6s5p3d]$ basis set optimized for the pseudopotential of Ref. 23. We decontracted one p and one d function, ending up with a $[6s6p4d]$ set which was supplemented with $2f1g$ polarization exponents optimized in CCSD calculations for the free ground-state atom (f exponents are 2.45, 0.766, and the g -exponent is 2.132).

B. SCF calculations

With the CRYSTAL95 program package^{21,22}, SCF energies for 100 different sets of randomly chosen a, c, x values were calculated. A region around the minimum was covered more densely. The computational results were fitted by a 3-variable polynomial of third order plus a few quartic terms which turned out to be significant. (Typically about twenty constants to fit.)

Some final results of SCF calculations are collected in Table I. We recover at the SCF level about 57 % (834 mH) of the experimental cohesive energy. The lattice constant is already close to experiment, but the bulk modulus turns out to be substantially too high. These results indicate the importance of taking into account electron correlation.

C. Correlation calculations

For the correlation calculations, we applied the coupled-cluster approach with single and double excitations (CCSD)²⁷ and included perturbatively triples (CCSD(T))²⁸ as implemented in the program package MOLPRO^{29,30}. Within the incremental scheme, we studied one-, two- and three-atom clusters. (For the three-atom clusters, we performed CCSD calculations only.) The clusters were embedded in a large slab of Madelung point charges ($7 \times 7 \times 9$ unit cells, charges +4 and -2, respectively), similarly as described in Refs.^{2,15,14,16}. An exception are the Ti ions nearest to the cluster atoms: in this case, Ti^{4+} pseudopotentials³¹ were used instead of the bare point charges, in order to simulate the Pauli repulsion on the O^{2-} electrons of the inner cluster. *The not fully ionic character of the system turns out to be the basic difficulty.* When doing computations on finite clusters, only an integer electron number is allowed and the atomic populations obtained from the CRYSTAL calculation cannot easily be reproduced as is the case for perfectly ionic systems. We are forced to assign to the clusters considered the same total electron charges as in hypothetical purely ionic Ti^{4+} , O^{2-} rutile. Of course, this is no issue in large clusters, but may be critical for

small ones. In order to control the quality of this approximation, we compare the results for the individual increments taken from clusters with one, two, and three explicitly described ions (see Table II).

The bulk of our correlation-energy calculations (whose results appear in Table I) was done for embedded clusters with one and two explicitly treated atoms. The maximum distance between the atoms within these clusters was up to 8 atomic units. These clusters (altogether 13 in number) provide us with the most significant one-body and two-body contributions to E_{corr} . For 5 different geometries, all these increments were calculated. For 15 other geometries, the 8 most important increments were explicitly calculated whereas the remaining 5 least important (contributions below 1 mH) were obtained by interpolation. To estimate the importance of three-body contributions, we also calculated the biggest three-body $O - Ti - O$ increments for one geometry, and they were found to be of the order of 1 mH.

A very important question is the transferability of these increments from one type of cluster to the other (see Table II). In every case, our increments refer to localized orbital groups which can be formally attributed to O^{2-} and Ti^{4+} ions, respectively, but due to partially covalent bonding in TiO_2 , especially the former orbital group becomes more delocalized when going to larger clusters. Specifically, we see that the oxygen correlation energy increases in magnitude when taken from a cluster with three explicitly described ions (one titanium ion, two oxygen ions, to be consistent with the formula unit) instead of out of a cluster where only the oxygen ion has basis functions. We explain this with a better description of the diffuse tail of the oxygen charge, as the charge is allowed to flow to the titanium ion. The more diffuse ion has lower-lying excitations which explains the change of the correlation energy. In the same way, we can compare the titanium correlation energy of a cluster where only one titanium ion has basis functions to that of a cluster with three explicitly described ions. We find that the titanium correlation energy is reduced in magnitude. This is due to the oxygen charge which has flown to the titanium ion and has led to a d occupancy. Excitations of the $3s$ and $3p$ electrons into d orbitals are now (partially) forbidden, i.e., we have an exclusion effect. In total, both effects almost cancel for the one-body increments ($|\Delta\epsilon(O)|$ increases by 5 mH, to be multiplied with a weight factor of 4, $|\Delta\epsilon(Ti)|$ decreases by 11 mH, to be multiplied with 2). For the two-body increments, a partial cancellation with increasing cluster size takes place, too: O-O increments are enhanced by ~ 4 mH when bridging Ti atoms are taken into account, while Ti-O increments are reduced in magnitude by ~ 3 mH in the TiO_2 unit³².

As a whole, we find that the transferability is reasonable but rather poor in comparison to purely ionic crystals where cluster charges are strictly confined (see Table II). This is not unexpected as the *perfect-ion approximation* is broken in a different way for each of the clusters studied. To overcome this transferability problem, the

only way would be to further improve the cluster surroundings by using more than three explicitly described ions with high quality basis set (ideally in multiples of the formula unit), which is presently not possible because of the steeply increasing computational effort.

The correlation energies obtained this way were fitted for 20 geometries by a second-order polynomial (ten parameters), analogously as previously described for SCF energies. Adding the two resulting formulae, we obtained $E_{tot}(a, c, x)$ so that we could perform the calculation of physical constants which include correlation effects (see Table I).

III. DISCUSSION AND SUMMARY

As SCF and SCF+CCSD(T) lattice constants are not very different and both rather close to the experimental values we conclude that electron correlations do not influence the crystal geometry in a major way. The technical explanation is provided by studying the coefficients of the analytic (fitted) formula of $E_{corr}(r_1, r_2, \theta)$, in atomic units, at the CCSD(T) level:

$$\begin{aligned} E_{corr}(r_1, r_2, \theta) \approx & -2.1241 - 0.0121\Delta r_1 \quad (6) \\ & -0.0067\Delta r_2 - 0.0322\Delta\theta \\ & +0.2570(\Delta r_1)^2 - 1.5730(\Delta r_2)^2 - 1.2490(\Delta\theta)^2 \\ & -3.0459\Delta r_1\Delta r_2 + 1.3580\Delta r_1\Delta\theta - 0.0875\Delta r_2\Delta\theta \end{aligned}$$

The normalized dimensionless expansion variables are defined as $\Delta r_1 = (r_1 - r_{10})/r_{1exp}$ where r_{10} is the SCF equilibrium value of the internal variable r_1 and r_{1exp} is the corresponding experimental value. Analogous expressions hold for Δr_2 and for $\Delta\theta$. The coefficients of the linear terms are much smaller than the coefficients of the quadratic terms. This explains why the compressibility is strongly renormalized by correlations as it depends primarily on the coefficients of the quadratic term.

To understand this situation it is necessary to study how individual increments change when the lattice constants change. To gain a qualitative understanding it is enough to study the biggest contributions: the one-body increment for oxygen and the two-body nn Ti-O increments. (Note that the one-body increment for Ti can be considered as constant, to a good approximation). In the following we will describe several competing mechanisms which cause linear changes of the bulk correlation energy to be small near the SCF minimum.

Let us start with oxygen (one-body increment for oxygen). Its change as a function of the lattice constant is in part of intraatomic origin and in part of electrostatic origin. First let us consider the intraatomic part. As found and explained in earlier work^{14,15,2}, excitations cost less energy when the lattice constant (and the volume of the quantum well enclosing the oxygen ion) increases; in that case, the magnitude of the correlation energy increases,

too. There is an opposite trend connected with the permanent electric field \vec{E} at the oxygen site. As the lattice expands, the Madelung field decreases, and the influence of correlation on the static polarization of the oxygen ions, $\frac{1}{2}(\alpha_{SCF} - \alpha_{corr})\vec{E}^2$ (with polarizabilities α_{SCF} and α_{corr} at SCF and correlated levels, respectively), decreases in parallel. (Note that due to symmetry there is no static electric field at the site of the Ti ions). A competition between the two effects just described apparently leads to a relatively small change in the total oxygen correlation energy as a function of the lattice constant.

Thus, the most important source of variability are two-body increments. For the two-body nn Ti-O increments, we find two competing effects again. To fix the attention let us provide two greatly simplified formulae (atomic units):

$$\begin{aligned}\Delta\varepsilon_{api} &\approx -0.027 + 0.083\Delta r_1 - 0.039\Delta r_2 - 0.036\Delta\theta \dots \quad (7) \\ \Delta\varepsilon_{equa} &\approx -0.026 - 0.046\Delta r_1 + 0.018\Delta r_2 + 0.040\Delta\theta \dots\end{aligned}$$

where $\Delta\varepsilon_{api}$ and $\Delta\varepsilon_{equa}$ are two-body nn Ti-O increments for apical and equatorial oxygen ions, respectively. The large quadratic terms in the above formulae were not shown as they are irrelevant to the following arguments. Let us remember that the multiplying weight factors (per unit cell) for $\Delta\varepsilon_{api}$ and $\Delta\varepsilon_{equa}$ are 4 and 8, respectively. Due to the opposite signs and due to the fact that the different linear term amplitudes are roughly in 1:2 proportion we may conclude that a small lattice distortion can change the individual $\Delta\varepsilon$ but not the sum $4\Delta\varepsilon_{api} + 8\Delta\varepsilon_{equa}$ which is roughly constant (but only in linear approximation). Thus, $4\Delta\varepsilon_{api} + 8\Delta\varepsilon_{equa}$ (and consequently the total correlation energy as well) is characterized by *small linear terms* and by *large quadratic terms*. The physical explanation is given by a competition between the bonds Ti - apical O and Ti - equatorial O. Suppose we distort the crystal in such a way that only the internal coordinate r_1 increases. The apical oxygens are a little further apart and the interatomic van der Waals-like correlation energy contained within $\Delta\varepsilon_{api}$ decreases in magnitude. At the same time, the polarizing influence of the Ti ions on the charge clouds of the apical oxygen anions decreases; this leads to a charge displacement from these anions towards their other Ti neighbours, with respect to which they are in equatorial positions, and, as a result, the electron correlation contained in $|\Delta\varepsilon_{equa}|$ is getting bigger. Analogous effects (of opposite sign) arise with a change of r_2 , with the exception that the two equatorial Ti neighbours of an oxygen anion are moved simultaneously, which leads to a smaller prefactor of Δr_2 , in the expression for $\Delta\varepsilon_{equa}$, as compared to that of Δr_1 for $\Delta\varepsilon_{api}$. The two discussed types of correlation-energy change are opposite and in linear approximation almost cancel.

In conclusion we have shown that electron correlations do not change the lattice geometry in a major way but are important for other ground-state properties — the cohesive energy and bulk compressibility which we ob-

tained are close to the experimental values. In view of these results, we conclude that the application of the incremental scheme to rutile yields new insights (in spite of the fact that we were forced to go to approximations which are problematic from the methodological point of view). In addition we gained valuable experience about how to apply this scheme to mixed covalent-ionic systems with fractional ion charges.

ACKNOWLEDGMENTS

We would like to thank Dr. M. Dolg, of the MPI-PKS (Dresden), for valuable discussions.

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TABLE I. Ab initio results for rutile

	SCF ^a	SCF ^b	SCF present work	SCF + CCSD(T)	experiment
a_0^c	4.559	4.555	4.529	4.548	4.592
c_0^c	3.027	3.024	3.088	2.993	2.958
x_0	0.3048	0.3061	0.3052	0.3046	0.3048
B^d	2.81	2.79	3.04	2.36 ^f	2.39
B_{ISO}^d	3.09	3.08	3.15	2.45	-
ΔE_B^e	1.025	1.175	0.834	1.422	1.470

^a Ref. 4 data (all-electron calculations)

^b Ref. 4 data (pseudopotentials on Ti and O)

^c units are Å

^d units are *Mbar*

^e ΔE_B is cohesive energy per unit cell; in Hartree units, including zero point vibrations with a Debye approximation and a Debye temperature of 530 K³³; the energies of the free atoms are averaged over J with the appropriate experimental spin-orbit contributions³⁴)

^f The estimated error bar for B is ± 0.06

TABLE II. Selected correlation-energy increments in rutile, from CCSD calculations (SCF equilibrium geometry from Ref. 4, 2nd column in Table I; atomic units). For the free atoms, we obtain correlation energies of -0.1714 H for O, and -0.4040 H for Ti, at the CCSD level.

	cluster	increment	weight factor per unit cell
$\Delta\varepsilon(O)$	O	-0.2613	4
	Ti-O ^a	-0.2692	
	Ti-O ^b	-0.2692	
	O-O ^c	-0.2607	
	O-Ti-O ^d	-0.2667	
	O-Ti-O ^e	-0.2666	
	Ti-O-Ti ^f	-0.2736	
$\Delta\varepsilon(Ti)$	Ti	-0.3117	2
	Ti-O ^a	-0.3054	
	Ti-O ^b	-0.3052	
	O-Ti-O ^d	-0.3009	
	O-Ti-O ^e	-0.3006	
	Ti-O-Ti ^f	-0.3062	
$\Delta\varepsilon(Ti - O_{api})^a$	Ti-O ^a	-0.0223	4
	O-Ti-O ^d	-0.0195	
	Ti-O-Ti ^f	-0.0200	
$\Delta\varepsilon(Ti - O_{equa})^b$	Ti-O ^b	-0.0239	8
	O-Ti-O ^d	-0.0206	
	O-Ti-O ^e	-0.0204	
	Ti-O-Ti ^f	-0.0208	
$\Delta\varepsilon(Ti - Ti)^g$	Ti-Ti ^b	-0.0001	2
	Ti-O-Ti ^f	-0.0001	
$\Delta\varepsilon(O - O)^c$	O-O ^c	-0.0051	2
	O-Ti-O ^e	-0.0093	
$\Delta\varepsilon(O - O)^h$	O-O ^h	-0.0029	16
	O-Ti-O ^d	-0.0066	
$\Delta\varepsilon(O - Ti - O)^d$	O-Ti-O ^d	+0.0012	16
$\Delta\varepsilon(O - Ti - O)^e$	O-Ti-O ^e	+0.0013	4
$\Delta\varepsilon(Ti - O - Ti)^f$	Ti-O-Ti ^f	+0.0001	4

^a Ti – nearest neighbour apical oxygen (distance - 3.72 a.u.)

^b Ti – nearest neighbour equatorial oxygen (distance - 3.70 a.u.)

^c nearest neighbour oxygen pair (distance - 4.72 a.u.)

^d equatorial oxygen – Ti – apical oxygen (distances: 3.72 and 3.70 a.u.)

^e equatorial oxygen – Ti – equatorial oxygen (distances: 3.70 and 3.70 a.u.; the O-Ti-O angle is 79°.)

^f Ti - O - Ti (distances: 3.72 and 3.70 a.u.)

^g nearest neighbour Ti-Ti pair (distance - 5.71 a.u.)

^h next nearest neighbour oxygen pair (distance - 5.25 a.u.)

FIG. 1. The rutile structure with oxygen (open circles) and titanium atoms (filled circles).

